LA-13658-MS

Approved for public release;
distribution is unlimited

Trace Elements, With Special Reference to Mercury, in Fish Collected Upstream and Downstream of Los Alamos National Laboratory

Los Alamos
NATIONAL LABORATORY

Los Alamos National Laboratory is operated by the University of Califo
for the United States Department of Energy under contract W-7405-EI

Edited by Hector Hinojosa, Group CIC-1

An Affirmative Action/Equal Opportunity Employer

LA-13658-MS

Issued: November 1999

Trace Elements, With Special Reference to Mercury, in Fish Collected Upstream and Downstream of Los Alamos National Laboratory

P. R. Fresquez
J. D. Huchton
M. A. Mullen

Los Alamos
NATIONAL LABORATORY
Los Alamos, New Mexico 87545

TRACE ELEMENTS, WITH SPECIAL REFERENCE TO MERCURY, IN FISH COLLECTED UPSTREAM AND DOWNSTREAM OF LOS ALAMOS NATIONAL LABORATORY

by

P.R. Fresquez, J.D. Huchton, and M.A. Mullen

ABSTRACT

Trace elements (Ag, As, Ba, Be, Cr, Cd, Cu, Hg, Ni, Pb, Sb, Se, and Tl) were determined in muscle (fillet) of average sized fish (mostly carp, catfish, and sucker) collected from the confluences of major canyons that cross Los Alamos National Laboratory (LANL) lands with the Rio Grande (RG). Also, trace elements were determined in fish from reservoirs upstream (Abiquiu [AR]) and downstream (Cochiti [CR]) of LANL from 1991 through 1999. In general, all of the (mean) trace elements, including Hg, were either at the limits of detection (LOD) or in low concentrations at all study sites. Of the trace elements (e.g., Ba, Cu, and Hg) that were found to be above the LOD in fish muscle collected from LANL canyons/RG, none were in significantly higher ($p < 0.05$) concentrations than in muscle of fish collected from background locations. Mercury concentrations (mean of means) in fish from AR (all other trace elements were at LOD) were significantly higher ($p < 0.10$) than Hg concentrations in fish from CR, and Hg concentrations in fish collected from both reservoirs exhibited significantly (AR = $p < 0.05$ and CR = $p < 0.10$) decreasing trends over time.

I. INTRODUCTION

During the early years of Los Alamos National Laboratory (LANL) operations (early 1940s), some canyon drainage systems, which are major pathways for contaminants to reach off-site receptors, received various amounts of untreated waste effluents (Purtymun, 1974; Hakonson et al., 1980; Fresquez et al., 1995; Bennett et al., 1996). As a result, some of these canyons contain small amounts of light, heavy, and nonmetal trace elements, including mercury (Hg) (Hakonson et al., 1980). Although most of the runoff and/or effluent flow in the canyons is lost to the underlying alluvium and to evapotranspiration before leaving LANL lands (Stevens et al., 1993), some flow from excessive storm events may reach the Rio Grande (RG) (Abeele et al., 1981). The RG is the main tributary in New Mexico (NM) and traverses approximately 750 river miles from its headwaters in the San Juan Mountains in southwestern Colorado, through the State of NM, to El Paso, Texas, and beyond to the Gulf of Mexico (Ellis et al., 1993).

Mercury concentrations in fish occurring in rivers, lakes, and reservoirs in NM have been of significant concern to the public for a number of years (Torres, 1998); there are currently 26 fish advisories for Hg in NM waters based on the 1 ppm wet weight (w w) limit (NMDH, 1993). The main source of Hg into water systems is from atmospheric deposition resulting from natural degassing of the earth's crust (2,700 to 6,000 tons of Hg annually) and burning of fossil fuels (2,000 to 3,000 tons of Hg annually) (Foulke, 1994). Although the concentration of Hg in all but a few small, often ephemeral, rivers and streams in NM are very low (NMED 1999), inorganic Hg existing in the water is converted to methyl mercury $(CH_3)Hg^+$, a neurotoxin, under anaerobic conditions by sulfate reducing bacteria (Driscoll et al., 1994; Bunce 1991). Methyl mercury is fat and water soluble, which is easily taken up by living cells (Hammond and Foulkes, 1986); it is the main form of Hg in fish (95%) (Driscoll et al., 1994); and it bioaccumulates (e.g., larger fish > smaller fish) (Bache et al., 1971) and biomagnifies (e.g., carnivorous fish > omnivorous fish > herbivorous fish) readily (Ochiai 1995).

As part of the environmental surveillance program at LANL, fish are collected annually upstream and downstream of LANL for the analysis of radionuclides and nonradionuclides (light, heavy, and nonmetal trace elements) (polychlorinated biphenyls have also been analyzed, albeit on a one time basis, and are reported eleswhere [Gonzales et al., 1999]). This information is used in an effort to ascertain the effects of Laboratory operations on the human food chain (ESP 1999). The purpose of this paper is to summarize trace elements, with particular reference to Hg, in muscle (fillet) tissues of average size fish (mostly carp, catfish, and suckers) collected at Abiquiu reservoir (AR), which is upstream of LANL, and at Cochiti reservoir (CR), which is downstream of LANL, from 1991 through 1999. Also, a previous study involving the determination of trace elements in fish collected at the confluences of major canyons that cross LANL lands with the RG (Fresquez et al., 1999) are presented for comparison and reference.

II. MATERIALS AND METHODS

Two studies were conducted. In the first study, four to five fish (16 to 18 inches in length) consisting of white sucker (*Catostomus commersoni*), catfish (*Ictalurus punctatus*), and carp (*Cyprinus carpio*) were collected using a raft-mounted Smith-Root Electrofisher shocking device along the RG starting at San Ildefonso (SI) (approximately one mile upstream from any intermittent streams that cross LANL lands) and then from the confluences of Los Alamos Canyon (LAC), Mortandad Canyon (MC), Pajarito Canyon (PC), and Frijoles Canyon (FC) (Fresquez et al., 1999) (Figure 1).

The second study involved collecting the same species of fish collected in study one, albeit smaller (most fish, with the exception of the crappie [4 to 7 inches long], ranged in size from 12 to 14 inches in length), from AR and CR. AR (4,290 acres in size) is located on the Rio Chama approximately 40 miles upstream of LANL, and CR, an 11,000-acre flood and sediment control project, is located on the RG approximately eight miles downstream of LANL. The fish were collected with gill nets, and the number and type of fish collected from the reservoirs from 1991 through 1999 were the following: 1991, AR = 6 (4 catfish, 2 brown trout [*Salmo trutia*]), CR = 7 (5 white crappie [*Pomixis annularis*], 2 catfish); 1994, AR = 7 (catfish), CR = 7 (catfish); 1995, AR = 5 (catfish), CR = 5 (catfish); 1996, AR = 5 (catfish), CR = 5 (catfish); 1997, AR = 5 (2 catfish, 1 white sucker, 2 carp), CR = 5 (1 catfish, 1 white sucker, 3 carp); 1999, AR = 6 (3 catfish, 1 white sucker, 2 carp), CR = 5 (1 catfish, 1 white sucker, 3 carp).

All fish were placed into large plastic bags following collection, marked for identification, and transferred to LANL in an ice chest cooled to 4°C. In the laboratory, a subsample (~25 g wet) of muscle (fillet) from each fish was placed into a quart

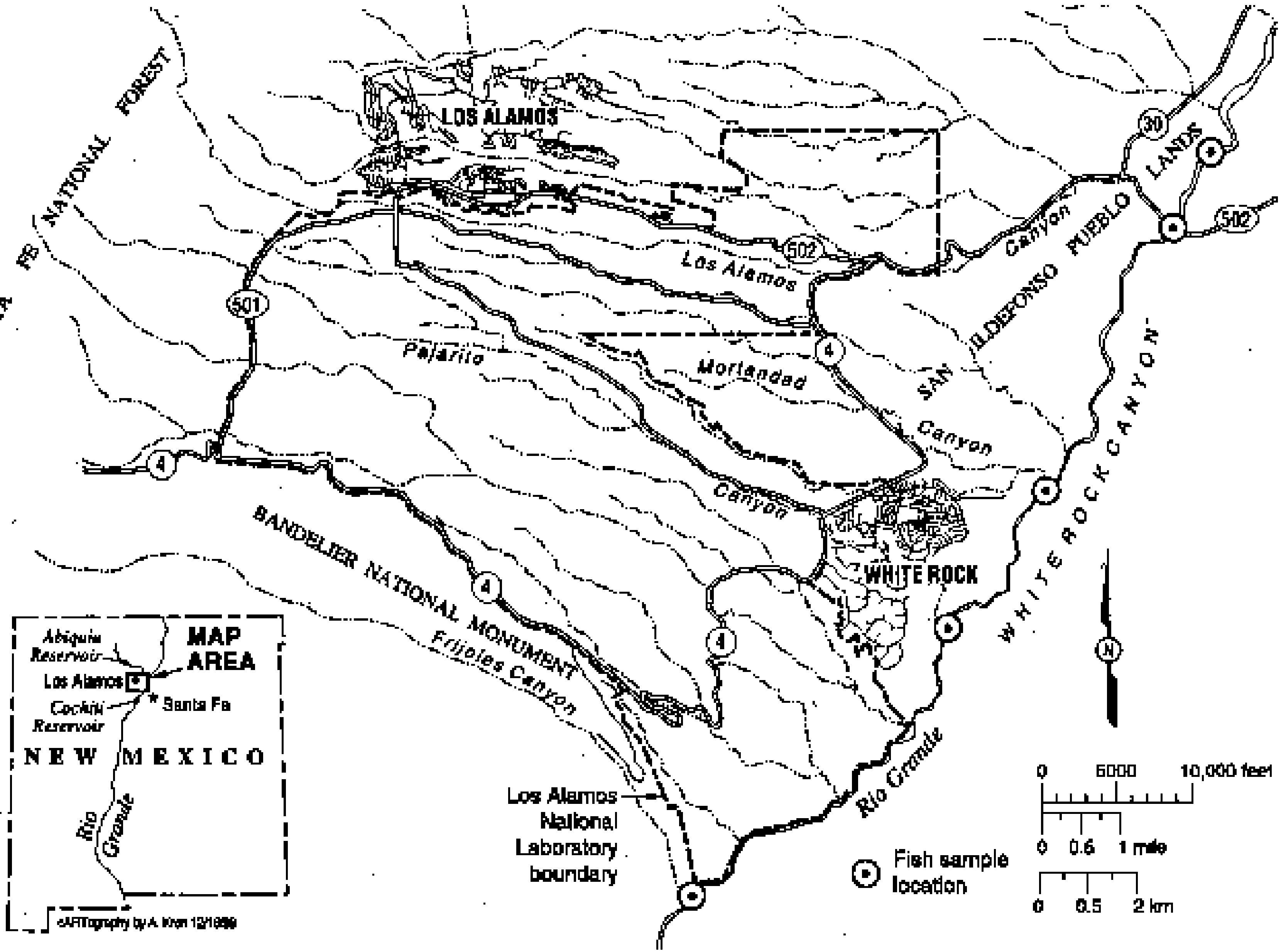

Figure 1. Locations of sites along the Rio Grande where fish were collected.

size Ziplock plastic bag and submitted to the Chemical Science and Technology group (samples from AR and CR in 1991 were submitted to the NM Scientific Laboratory Division, Air and Heavy Metals Section, Albuquerque, NM) for analysis of light, heavy, and nonmetal trace elements: Ag, As, Ba, Be, Cr, Cd, Cu, Hg, Ni, Pb, Sb, Se, and Tl. All methods of trace element analyses in fish have been described previously (Fresquez et al., 1994; Fresquez et al., 1996). Results are reported in $\mu g\ g^{-1}$ w w.

Variations in the mean trace element content in muscle between AR and CR and between SI/RG and LAC/RG, MC/RG, PC/RG, and FC/RG were assessed using a Wilcoxon Rank Sum Test at the 0.05 and 0.10 probability level (Gilbert, 1987). Trend analysis for Hg concentrations over a nine-year period was completed using a Mann-Kendal test at the 0.05 and 0.10 probability level.

III. RESULTS AND DISCUSSION

Most trace element concentrations in muscle from fish collected from the confluences of LANL canyons with the RG were below the limits of detection (LOD) (Fresquez et al., 1999). Of the trace elements that were above the LOD (Ba, Cu, and Hg), none of these trace metals in fish collected from the LANL canyons/RG were in significantly higher ($p < 0.05$) concentrations than trace metals in fish collected upstream of LANL at SI/RG (background) (Table 1). Mean Hg concentrations, in particular, ranged from 0.16 to 0.21 $\mu g\ g^{-1}$ w w (the highest individual Hg level [0.27 $\mu g\ g^{-1}$ w w] was detected in a carp at the FC/RG confluence) and were well within the 0.5 μg Hg g^{-1} w w limit that is widely accepted as representative of natural Hg levels in fish of unpolluted fresh water systems (Abernathy and Cumbie, 1977) and below the United States Food and Drug Administration's (USFDA) ingestion limit of 1 μg Hg g^{-1} w w (Torres, 1998).

Most trace elements, with the exception of Hg, in fish collected from AR and CR over a nine-year period were below the LOD (ESP 1993, 1996a, 1996b, 1997, 1998, and n.d.). In general, mean Hg concentrations in all years in fish from AR, upstream of LANL, were generally higher than Hg concentrations in fish from CR, and the statistical analysis of the mean of means showed that Hg in fish from AR was significantly higher ($p < 0.10$) than Hg in fish collected from CR (Table 2). The highest individual Hg concentrations [1.0 $\mu g\ g^{-1}$ w w] were detected in a single catfish each from AR and CR in 1994, and the only carnivourous fish collected, brown trout from AR and white crappie from CR in 1991, contained 0.30 and 0.36 $\mu g\ g^{-1}$ w w of Hg, respectively. As with the fish collected from the RG, albeit with some notable (individual) exceptions, mean concentrations of Hg in fish from both AR and CR were within Hg concentrations typical of fish from nonpolluted fresh water systems (Abernathy and Cumbie, 1977) and below the USFDA's ingestion limit of 1 μg Hg g^{-1} w w (Torres, 1998). Concentrations of Hg in catfish from this study were very similar to Hg levels in catfish recently collected from Conchas (averaged 0.25 $\mu g\ g^{-1}$ w w) and Santa Rosa (ranged from 0.22 to 0.33 $\mu g\ g^{-1}$ w w) lakes (Bousek, 1996; Torres, 1998); and, these authors concluded that health risks to the average sport fisherman posed by Hg in fish from Conchas and Santa Rosa lakes were negligible.

Overall, mean Hg concentrations in fish collected from both reservoirs show significantly decreasing trends over time; AR ($p = 0.045$) was significant at the 0.05 probability level and CR ($p = 0.066$) was significant at the 0.10 probability level. It is not completely known why concentrations of Hg are decreasing in fish collected from AR and CR, but the reduction of emissions in coal-burning power plants and/or the reduction of carbon sources within the reservoirs may be but two of the reasons. Since the early 1980s, for example, coal burning power plants in the northwest corner of NM have been required to install benturi scrubbers and bag houses to capture particulates and reduce air emissions (Paul Martinez, personnel communication, Environmental Engineer Specialist, Air Quality Bureau, New Mexico Environment Department, September 22, 1999). Additionally, since the conversion of Hg to methyl mercury is primarily a biological process, it has been demonstrated that Hg concentrations in fish tissue rise significantly in impoundments that form behind new dams, and then gradually decline to an equilibrium level as the carbon provided by flooded vegetation is depleted (NMED 1999).

IV. CONCLUSIONS

Most concentrations of trace elements, including Hg, in fish collected from the RG, as it passes on the eastern edge of LANL and at CR (with some notable exceptions) were either at LOD or low. Because Hg concentrations in fish collected from upstream areas of LANL showed higher levels than downstream areas, the amounts of Hg in fish inhabiting the RG and CR were mostly a result of either natural and/or anthropogenic sources other than LANL. In any case, concentrations of Hg in fish collected from both reservoirs showed significantly decreasing trends over time.

V. ACKNOWLEDGMENTS

We would like to thank the United States Fish and Wildlife Service, Department of Interior, for sampling and boating support for the LANL canyons/RG study—assistance by Joel Lusk, Sky Bristol, Zack Simpson, and Mark Wilson was very much appreciated. Also, we would like to thank Johnnye Lewis, representing San Ildefonso Pueblo; William DeRegan, Corp of Engineers at Cochiti Reservoir; Audrey Hayes, LANL Graduate Research Assistant; Joy Ferenbaugh, LANL Graduate Research Assistant; and Paul Torrez, LANL Undergraduate Student, for participating in sampling, laboratory processing, and/or general study site support.

Table 1. Mean (±std dev) trace elements (µg/g w w) in muscle of fish collected from the Rio Grande upstream and downstream of LANL.[1]

Location	Ba	Cu	Hg
SI/RG (BG)	0.49 (0.41)a[2]	0.90 (0.42)a	0.21 (0.03)a
LAC/RG	1.05 (1.50)a	0.54 (0.34)a	0.17 (0.03)a
MC/RG	0.35 (0.15)a	0.68 (0.12)a	0.16 (0.06)a
PC/RG	1.36 (1.42)a	0.68 (0.56)a	0.16 (0.04)a
FC/RG	0.54 (0.46)a	0.75 (0.18)a	0.21 (0.05)a

[1]Data from Fresquez et al., 1999.
[2]Means within the same column followed by the same lower case letter were not significantly different at the 0.05 probability levels using a nonparametric Wilcoxon Rank Sum test.

Table 2. Mean (±std dev) mercury (µg/g w w) in muscle of fish collected from reservoirs upstream and downstream of LANL from 1991 through 1999.

Year[1]	Abiquiu Reservoir	Cochiti Reservoir
1991	0.35 (0.09)a[2]	0.35 (0.12)a
1994	0.37 (0.28)a	0.28 (0.32)a
1995	0.34 (0.26)a	0.12 (0.05)a
1996	0.34 (0.10)a	0.21 (0.10)a
1997	0.16 (0.10)a	0.15 (0.10)a
1999	0.24 (0.12)a	0.14 (0.09)a
Mean of Means (±SD)	0.29 (0.09)A[3]	0.18 (0.07)B

[1]1991 analyzed by the NM Scientific Laboratory Division and 1994 to 1999 analyzed by LANL laboratory.
[2]Means within the same row followed by the same lower case letter were not significantly different at the 0.05 probability levels using a nonparametric Wilcoxon Rank Sum test.
[3]Means within the same row followed by the same upper case letter were not significantly different at the 0.10 probability levels using a nonparametric Wilcoxon Rank Sum test.

V. REFERENCES

Abeele, W.V., M.L. Wheeler, and B.W. Burton, "Geohydrology of Bandelier Tuff," Los Alamos Scientific Laboratory report LA-8962-MS (1981).

Abernathy, A.R., and P.M. Cumbie "Mercury Accumulation by Largemouth Bass in Recently Impounded Reservoirs," Bulletin of Environ Contamination and Toxicology, 17:595-602 (1977).

Bache, C.A., W.H. Gutenmann, and D.J. Lusk, "Residues of Total Mercury and Methylemercuric Salts in Lake Trout as a Function of Age," Science 172:951–952 (1971).

Bennett, K., J. Biggs, and P.R. Fresquez, "Radionuclide Contaminant Analysis of Small Mammals, Plants, and Sediments within Mortandad Canyon, 1994," Los Alamos National Laboratory report LA-13104-MS (1996).

Bousek, J., "An Analysis of Copper, Zinc, and Mercury Concentrations in Fish Species in Santa Rosa Reservoir, New Mexico," M.S. Thesis, New Mexico Institute of Mining and Technology, Socorro, NM (1996).

Bunce, N., *Environmental Chemistry*, Wuerz Publishing Ltd., New York, NY (1991).

Driscoll, C.T., C. Yan, C.L. Schofield, R.K. Munson, and J.G. Holsapple, "The Mercury Cycle and Fish in the Adirondack Lakes," Environmental Science and Technology, 28:136–143 (1994).

Ellis, S.R., G.W. Levings, L.F. Carter, S.F. Richey, and M.J. Radell, "Rio Grande Valley, Colorado, New Mexico, and Texas," Water Resource Bulletin, American Water Resources Association, 29:617–646 (1993).

ESP (Environmental Surveillance Program), "Environmental Surveillance at Los Alamos during 1991," Los Alamos National Laboratory report LA-12572-ENV (1993).

ESP (Environmental Surveillance Program), "Environmental Surveillance at Los Alamos during 1994," Los Alamos National Laboratory report LA-13047-ENV (1996a).

ESP (Environmental Surveillance Program), "Environmental Surveillance at Los Alamos during 1995," Los Alamos National Laboratory report LA-13210-ENV (1996b).

ESP (Environmental Surveillance Program), "Environmental Surveillance at Los Alamos during 1996," Los Alamos National Laboratory report LA-13343-ENV (1997).

ESP (Environmental Surveillance Program), "Environmental Surveillance at Los Alamos during 1997," Los Alamos National Laboratory report LA-13487-ENV (1998).

ESP (Environmental Surveillance Program), "Environmental Surveillance at Los Alamos during 1998," Los Alamos National Laboratory report LA-13633-ENV (1999).

ESP (Environmental Surveillance Program), "Environmental Surveillance at Los Alamos during 1999," Los Alamos National Laboratory report (unpublished data) (no date).

Foulke, J.E., "Mercury in Fish: Cause for Concern," Food and Drug Administration Consumer, September (1994).

Fresquez, P.R., D.R. Armstrong, and J.G. Salazar, "Radionuclide Concentrations in Game and Nongame Fish Upstream and Downstream of Los Alamos National Laboratory: 1981 to 1993," Los Alamos National Laboratory report LA-12818-MS (1994).

Fresquez, P.R., T.E. Foxx, and L. Naranjo, Jr., "Strontium Concentrations in Chamisa (*Chrysothamnus nauseosus*) Shrub Plants Growing in a Former Liquid Waste Disposal Area in Bayo Canyon," Los Alamos National Laboratory report LA-13050-MS (1995).

Fresquez, P.R., D.R. Armstrong, and L. Naranjo, Jr., "Radionuclide and Heavy Metal Concentrations in Soil, Vegetation, and Fish Collected Around and Within Tsicoma Lake in Santa Clara Canyon," Los Alamos National Laboratory report LA-13144-MS (1996).

Fresquez, P.R., D.H. Kraig, M.A. Mullen, and L. Naranjo, Jr., "Radionuclides and Trace Elements in Fish Collected Upstream and Downstream of Los Alamos National Laboratory and the Doses to Humans From the Consumption of Muscle and Bone," Journal of Environmental Science and Health Part B, B34 (5):885–900 (1999).

Gilbert, R.O., *Statistical Methods for Environmental Pollution Monitoring*, Van Nostrand Reinhold, New York, NY (1987).

Gonzales, G.J., P.R. Fresquez, and J.W. Beveridge, "Organic Contaminant Levels in Three Fish Species Downchannel from the Los Alamos National Laboratory," Los Alamos National Laboratory report LA-13612-MS (1999).

Hakonson, T.E., G.C. White, E.S. Gladney, and M. Dreicer, "The Distribution of Mercury, Cesium-137, and Plutonium in an Intermittent Stream at Los Alamos," Journal of Environmental Quality 9:289–292 (1980).

Hammond, P.B., and E.C. Foulkes, "Metal Ion Toxicity in Man and Animals," In: *Concepts in Metal Ion Toxicology*, Vol 20, Sigel, H., Ed., Marcel Dekker, Inc., New York, NY (1986).

NMDH (New Mexico Department of Health), "Fish Consumption Guidelines due to Mercury Contamination," NM Department of Health, NM Environment Department, NM Department of Game and Fish (1993).

NMED (New Mexico Environment Department), "A White Paper on Mercury," New Mexico Environment Department, Surface Water Quality Bureau, Santa Fe, NM (1999).

Ochiai, E., "Toxicity of Heavy Metals and Biological Defense: Principles and Applications in Bioinorganic Chmistry-VII," Journal of Chemical Education, 72:479–484 (1995).

Purtymun, W.D., "Storm Runoff and Transport of Radionuclides in DP Canyon, Los Alamos County, New Mexico," Los Alamos Scientific Laboratory report LA-5744-MS (1974).

Stevens, D.B., P.M. Kearl, and R.W. Lee, "Hydrogeologic Review for the Environmental Restoration Program at Los Alamos National Laboratory," LANL Hydrogeology Panel Final Report, Daniel B. Stephens and Associates, Inc., Albuquerque, NM (1993).

Torres, P., "Metal Accumulation in Various Fish Species from Conchas Lake and Santa Rosa Lake in East Central New Mexico," M.S. Thesis, New Mexico Institute of Mining and Technology, Socorro, NM (1998).

Los Alamos
NATIONAL LABORATORY
Los Alamos, New Mexico 87545